Fuel Property Model Transfer for Fielded Near-infrared Spectrometers

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ABSTRACT

Fuel theft in the form of diluting shipments using less expensive petroleum products continues to grow globally. Consequently, there exists a need to rapidly verify fuel quality during change of custody. Ideally such verification not only includes the fuel type: diesel, gasoline, or jet, but also their associated specification properties. Unfortunately, such verification must often be performed far from a lab containing standard fuel analysis instruments and apparatus. We have addressed this need by developing a portable fuel property analyzer based on Near-Infrared Spectroscopy that employs multivariate statistics to determine numerous properties in less than 10 seconds using only 2 mL of sample. These properties include: octane of gasoline and cetane of diesel; aromatic & saturate content; distillation, flash, freeze point, pour point; density (API gravity), Reid vapor pressure, viscosity, hydrogen content, and net heat. Here we describe the method to transfer the property models from a master analyzer to slave analyzers in accordance to ASTM practices.

BACKGROUND

A portable near-infrared spectrometer was designed and built to measure multiple fuel properties. The instrument was designed to MIL-SPEC requirements to be rugged and operate over wide temperature range (-25 to +135 F). The rugged design was achieved using state of the art components and no moving parts. To preserve the calibration model, an effective model transfer method is necessary because the original fuel samples are volatile and not stable in the storage containers over a long period of time. For this reason, model transfer from the a master instrument to slave instruments is important.

Table 1. Fuel Properties Measured by the PFPA

Diesel	Jet Fuel	Gasoline
Density / API Gravity	Density / API Gravity	Density / API Gravity
Distillation Fractions (IBP, 10%, 50%, 90%, FBP)	Distill Fractions (IBP, 10%, 50%, 90%, FBP)	Distill Fractions (IBP, 10%, 50%, 90%, FBP)
Cetane Index	Cetane Index	Octane (RON, MON, AKI)
Viscosity (+40 C)	Viscosity (-20C, +40C)	Reid Vapor Pressure
Flash Point	Flash Point	Ethanol
Cloud Point	Freeze Point	MTBE
Aromatics / Saturates	FIS-II	Benzene, Toluene, Ethylbenzene, Xylenes
Biodiesel Content	Aromatics	
	Hydrogen Content	
	Net Heat	

Figure 1. PFPA

OBJECTIVES

- From a master instrument using fuel samples obtained around the world, build robust multivariate calibration models according to ASTM E1655 to predict multiple fuel properties.
- Validate calibration models using an independent dataset of fuel samples.
- Develop model transfer to standardize spectra collected on slave instruments.
- Transfer calibration models from the master instrument to slave instruments.
- Determine the performance of the model transfer on the slave instrument(s) using validation samples.

METHODS

- Multivariate models were created from a training set of 72 Jet Fuel samples that were obtained from around the world in accordance with ASTM E1655 using Partial Least Squares (PLS) on a Master instrument. See figure 1 as an example of a calibration model.
- Spectra used in the PLS models were preprocessed in the following manner: SNV, Savitzky-Golay 1st derivative 11-pt 2nd Order polynomial, Mean Centered.
- The PLS models were validated with a second set of 19 samples to determine model performance. These samples are also used to compare the performance of the predicted values on slaves instruments after the calibration transfer has been implemented.
- Calibration transfer was achieved by using Piece-wise Direct Standardization (PDS) to standardize the spectra collected on slave instruments. The purpose of this type of standardization is to correct the spectra obtained with a slave instrument to that of the master instrument so the models built on the master instrument can be used with a slave instrument. PDS is a commonly used method for calibration transfer, and it also considered a gold standard to which new transfer methods are compared with.
- Reference spectra for the PDS model consist of solvents which are the bulk components in the fuels. For diesel and jet fuel the following solvents are used: C8-14; and for gasoline: C5-C8, benzene, toluene, xylenes. Using solvents for model transfer allows the flexibility to calibrate future instruments without needed the original set of samples that can potentially change over time.
- 19 validation samples were used to determine model performance.

RESULTS

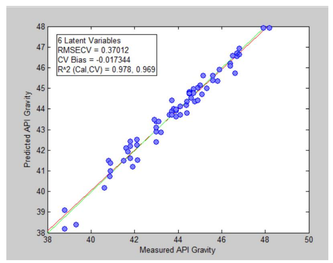

Figure 2

This is a typical model showing the measured vs predicted correlation of fuel property. All the calibration models are cross-validated using venetian-blinds to obtain the RMS Error (RMSECV) which is an indication of the model accuracy for predicting similar unknown samples.

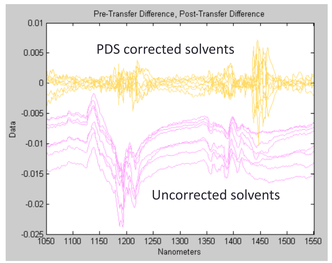

Figure 3.

The same set of solvent spectra are collected on both the Master instrument and Slave instrument. The PDS calibration transfer model is used to correct spectra collected on slave instruments. The corrected spectra from the slave instruments can then be used with the original model(s) developed on the Master instrument.

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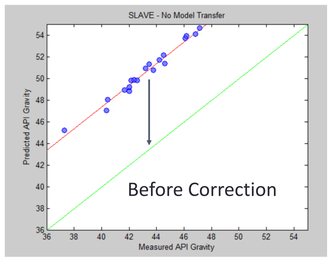

Figure 4

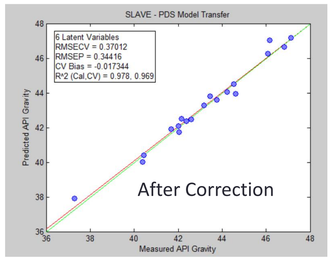

Figure 5

Figures 4 illustrates the impact predictions from a slave instrument without performing a calibration transfer (PDS instrument standardization). In this case, the predicted values for API Gravity have an offset of about 7 units. Figure 5 shows how well the models built on the master instrument can used with slave instrument(s) after the PDS calibration transfer has been implemented. Table 2 shows a detailed comparison of results for multiple fuel properties.

Table 2. Model Performance

			Master		Slave	
	ASTM	LV's	RMSECV	RMSEP	RMSEP	RMSEP
Model Transfer					PDS	None
API Gravity	D1298	6	0.37	0.38	0.34	7.39
Aromatic, V%	D1319	5	0.91	0.61	0.61	4.61
Cetane Index	D976	6	0.97	0.82	0.97	8.60
Density, kg/liter	D4052	5	2.3	1.6	1.4	26.2
Flash Point, C	D93	5	5.5	4.9	4.4	10.8
Freeze Point, C	D5972	5	3.3	3.7	3.6	18.0
Hydrogen Content	D3343	5	0.044	0.064	0.058	0.345
Net Heat	D3338	5	0.023	0.028	0.026	0.168
Saturate, V%	D1319	5	0.9	1.3	1.3	3.7
T10, C	D86	6	4.3	5.0	8.7	33.1
T50, C	D86	6	3.1	2.1	2.1	52.6
T90, C	D86	6	6.1	8.9	9.0	59.9
Viscosity(-20C)	D445	5	0.289	0.293	0.300	2.787

CONCLUSIONS

When transporting fuels it is important to verify that the fuel shipments meet required specifications. Often in the transportation process, the shipments pass through custody at different depots, pipelines and ports where the fuel properties should be quickly checked. To meet this need of testing multiple properties in the field, a rugged fuel analyzer based on near-infrared spectroscopy (NIRS) was developed.

Multivariate calibration models were developed on a Master instrument and a method of calibration transfer using Piece-wise Direct Standardization (PDS) was used to transfer the models to slave instrument. This rugged analyzer will be able to produce quick and accurate results correlated to ASTM methods for on-site fuel verification.